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Simultaneous Synthesis and Densification of Titanium Nitride/Titanium Diboride Composites by High Nitrogen Pressure Combustion

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Composites of TiN/TiB_2 were synthesized by a combustion process of BN, Ti in a nitrogen atmosphere. The effect of the BN/Ti ratio and the nitrogen gas pressure on the synthesis of these composites was investigated. Dense TiN/TiB_2 composites with relatively high hardness and toughness were fabricated by combustion synthesis from Ti and BN under a nitrogen pressure of 4.0 MPa. The Vickers microhardness of the products obtained from reactants with a BN/Ti mole ratio of 0.11 increased with an increase in nitrogen pressure and had a maximum value of ~25 GPa. Fracture toughness, K_{IC}, of the products increased from 3.1 to 5.9 MPa·m$^{1/2}$ as the BN/Ti ratio increased from 0.11 to 0.20. However, products formed under nitrogen pressures higher than 6.0 MPa exhibited circumferential macrocracks due to thermal shock.

I. Introduction

A VARIETY of high-temperature materials have been successfully synthesized by self-propagating combustion using solid–solid or solid–gas reactions.[1,2] An example of the latter is TiN, a material that has the attractive properties of relatively high hardness, high chemical stability and corrosion resistance, and high electrical conductivity.[3] However, products of combustion synthesis are generally porous and require further processing to obtain dense bodies.[4] Densification can be accomplished by such processes as hot pressing,[5] hot isostatic pressing,[6] explosive consolidation,[7] or hot-forging.[8]

TiN has been synthesized in porous form by reacting Ti with nitrogen gas under high pressure.[9,10] More recently, Shibuya *et al.*[11] achieved simultaneous combustion synthesis and densification of TiN under a nitrogen pressure of up to 10 MPa. The TiN products fabricated under a nitrogen pressure of 2–10 MPa were dense bodies, which maintained the shape of the initial specimen. It was observed that the nitrogen pressure had an effect on hardness and fracture toughness of the products. However, circumferential macrocracks were generated in the product due to thermal shock. To prevent cracking, the addition of controlled amounts of elemental nickel was found necessary. Products with a Ni/Ti mole ratio in the range of 0.1–0.6 were synthesized in dense form and were free of the circumferential macrocracks. The fracture toughness tended to increase with the content of nickel but the Vickers microhardness decreased correspondingly.

Another high-temperature material which has been prepared by combustion synthesis is TiB_2. It also possesses attractive properties of hardness, electrical conductivity, and chemical stability.[12] Thus the addition of TiB_2 to form TiN/TiB_2 composites has the potential of improving the hardness and toughness of TiN.[13–15] TiN/TiB_2 composites are useful in applications such as cutting tool and friction resistance materials. In the present work, we have investigated the synthesis of dense TiN/TiB_2 composites by a high-nitrogen-pressure combustion reaction between Ti and BN powders. In a recent work we have investigated the synthesis of dense TiN/TiB_2 nanocomposites using mechanical and field activation.[16]

II. Experimental Procedure

Powders of titanium, with an average particle size of about 22 μm and powders of BN with an average particle size of about 10 μm were used in this study. The titanium, obtained from Sumitomo SITIX, Inc. (Osaka, Japan), was reported to be 99.5% pure and the boron nitride powders were obtained from Kojundo Chemical Laboratory Co., Ltd. (Tokyo, Japan) and reported to be 99% pure. Powders of Ti and BN were weighed out in several mole ratios and were dry-mixed in an automated agate mortar for 0.5 h. From these mixed powders, cylindrical compacts, ~16 mm in diameter and 25 mm long, were formed in a stainless steel die with double-acting rams by uniaxial pressing at 3.0 MPa. Each compact was then placed in a porous crucible inside the combustion chamber. Details of the apparatus and the experimental methods have been provided in previous a publication.[11] An ignition device made of a slender carbon ribbon was placed on the top end of the compact. The chamber, which had a volume of 5.0×10^{-3} m^3, was evacuated and back-filled with nitrogen three times. Then it was filled with nitrogen to a pressure in the range of 0.1–10 MPa. The compact was then ignited by passing a current through the carbon ribbon.

The combustion synthesis reactions were videotaped at 30 frames per second (Sony CCD-V800 with a Kenko ND400 filter). The reaction temperature was monitored through a fused silica window with an optical pyrometer (Model IR-AQ, range 1000–3100°C, Chino, Inc.). The combustion wave velocity was measured with a video-measuring gauge (IV-560, For.A, Inc.). Following the synthesis process, products were polished with diamond powders and examined by scanning electron microscopy (SEM) (JSW-5200, JEOL) and analyzed by X-ray diffraction (RAD-C system, Rigaku, Inc.) using Cu$K\alpha$ radiation. For lattice parameter determinations, X-ray scans were made stepwise with $\Delta 2\theta = 0.02°$ and a collection time of 2 s using five peaks of the sample as well as the Si standard.

Hardness and fracture toughness of the products were determined by Vickers microhardness (HMV-2000, Shimazu, Inc.;

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load: 200 g; dwell time: 10 s) with indentation crack measurements.[17] Densities of the products were determined by the Archimedes method, except in cases of porous products, where the calculations were made based on weight and volume measurements.

III. Results and Discussion

(1) Effect of BN Addition under Constant Nitrogen Pressure

The use of hexagonal BN as a reactant was made to provide a solid source of nitrogen and thus minimize the problem of permeation-limited reactions with gaseous nitrogen.[10] The reaction conditions were changed by changing the amount of BN under a constant nitrogen pressure of 4.0 MPa. Figure 1(a) shows the effect of BN addition on the maximum combustion temperature and the combustion wave velocity. The maximum combustion temperature decreased from ~3100° to 2500°C as the molar ratio BN/Ti increased from 0 to 1.0. As will be seen later, the product of combustion contained the two phases TiB_2 and TiN only and thus the role of BN in the combustion reaction can be depicted as

$$y\text{Ti} + x\text{BN} + 0.5(y-1.5x)\text{N}_2 = 0.5x\text{TiB}_2 + (y-0.5x)\text{TiN} \tag{1}$$

The role of nitrogen in the above reaction depends on the ratio of BN/Ti ($=x/y$). Up to a ratio of $x/y = 0.67$, nitrogen gas is a reactant, but for higher ratios, it is a product. In the range of the ratio BN/Ti investigated in this work (0.11–1.0), the composites had a volume percent of TiB_2 ranging from 7.3% to 57.5%. Based on the reaction (1), the dependence of the adiabatic temperature on the BN/Ti ratio was calculated and the results are shown in Fig. 1(b). The calculations were made using the HSC software with its imbedded thermodynamic and thermophysical data.[18] The short plateau at 2920°C represents the melting point of TiB_2. Although one does not anticipate quantitative agreement between adiabatic and experimental temperatures, a qualitative trend is usually anticipated. However, this was not the case in this study. The calculated results showed a marked decrease in temperature with an increase in the BN/Ti ratio, while the experimental values showed only a modest decrease. Moreover, the measured temperature at BN/Ti = 1.0 was nearly 1500°C higher than the calculated value, 1093°C. This implies that the measured surface temperature was not a true representation of the combustion temperature but was dominated by a gas–solid reaction between Ti and nitrogen. The adiabatic temperature for this reaction was high, 4630°C.[2]

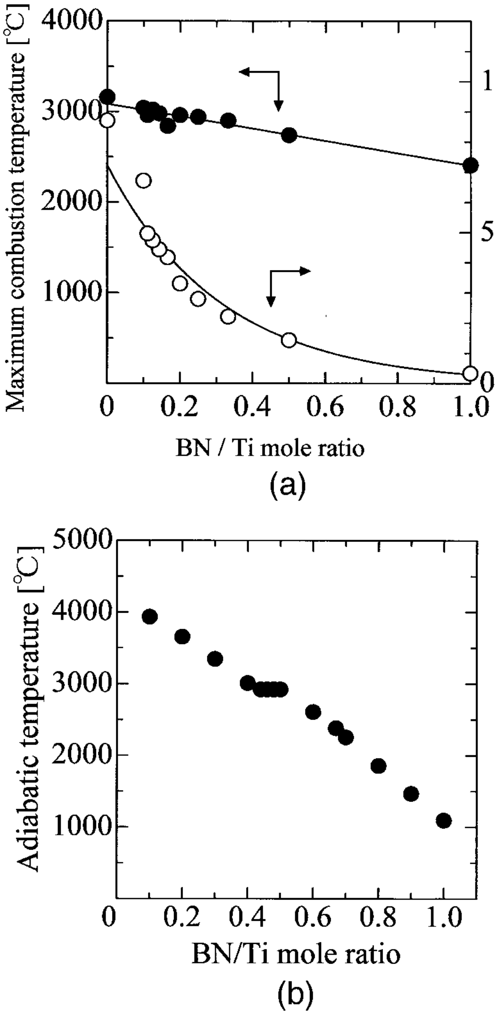

Fig. 1. (a) Effect of BN addition on the maximum combustion temperature and combustion wave velocity (nitrogen pressure: 4.0 MPa). (b) Effect of the BN/Ti ratio on the calculated adiabatic temperature.

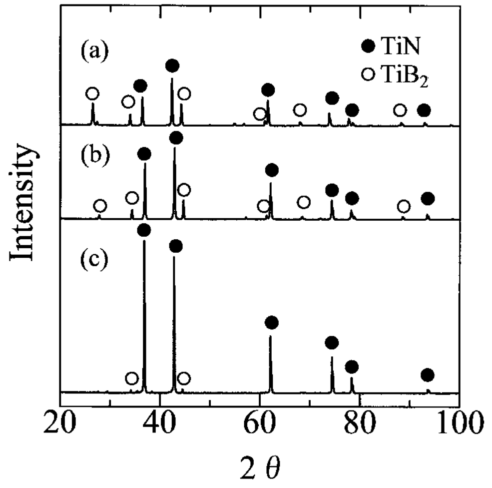

Fig. 2. XRD patterns of products formed from reactants with: (a) BN/Ti = 1.0, (b) BN/Ti = 0.33, (c) BN/Ti = 0.11 (nitrogen pressure: 4.0 MPa).

The combustion wave velocity decreased markedly with an increase in the BN/Ti ratio, as seen in Fig. 1(a). As the ratio increased from 0 to 1.0, the velocity decreased from about 85 to 3.0 $mm{\cdot}s^{-1}$. These results are more consistent with the trend in the calculated temperature, suggesting that the observed steady-state wave propagation was representative of the bulk reaction under a constant nitrogen pressure of 4.0 MPa and not the limited surface reaction influencing the measured temperature.

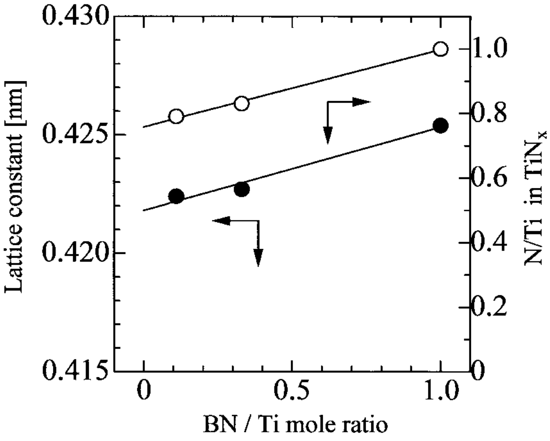

Fig. 3. Effect of BN/Ti ratio on the lattice constant and x of TiN_x in the products.

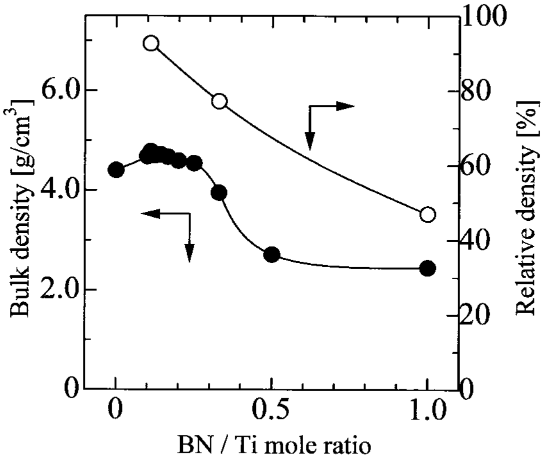

Fig. 4. Effect of BN/Ti ratio on the bulk relative densities of the products (nitrogen pressure: 4.0 MPa).

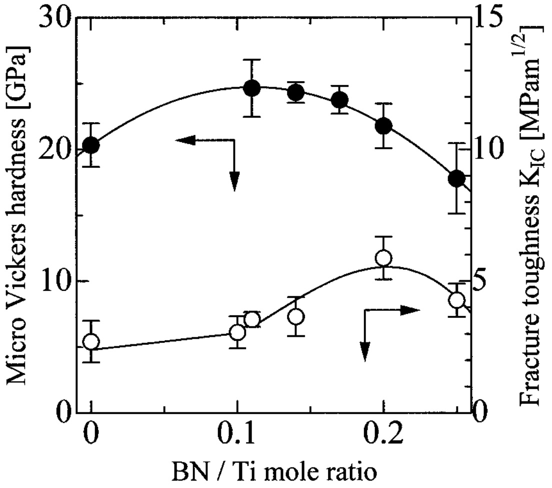

Fig. 6. Effect of BN/Ti ratio on the Vickers microhardness and fracture toughness K_{IC} of the products (nitrogen pressure: 4.0 MPa).

As indicated above, the products of combustion were found to contain TiN and TiB_2 only with no evidence for unreacted Ti. Figure 2 shows X-ray diffraction patterns of the products for reaction with BN/Ti ratios of (a) 1.0, (b) 0.33, and (c) 0.11. The relative peak intensity of TiB_2 decreased, expectedly, with a decrease in this ratio. As a phase, TiN_x is stable over a wide range of nitrogen stoichiometry and its lattice parameter depends correspondingly on composition.[19] From the published relationship and our XRD results, we calculated the effect of the BN/Ti mole ratio on the lattice constant and x in TiN_x of the products as shown in Fig. 3. The ratio of Ti/N increased toward the stoichiometric ratio as the amount of BN in the reactants increased. This observation supports the concept that BN is acted as a (solid) source of nitrogen. The phase in the product with a BN/Ti ratio of 0.11 was $TiN_{0.79}$.

The BN/Ti ratio influenced the final and relative densities of the products based on Eq. (1), as shown in Fig. 4. The product with no BN additive had circumferential macrocracks. However, the products with BN/Ti ratios in the approximate range 0.10−0.25 were

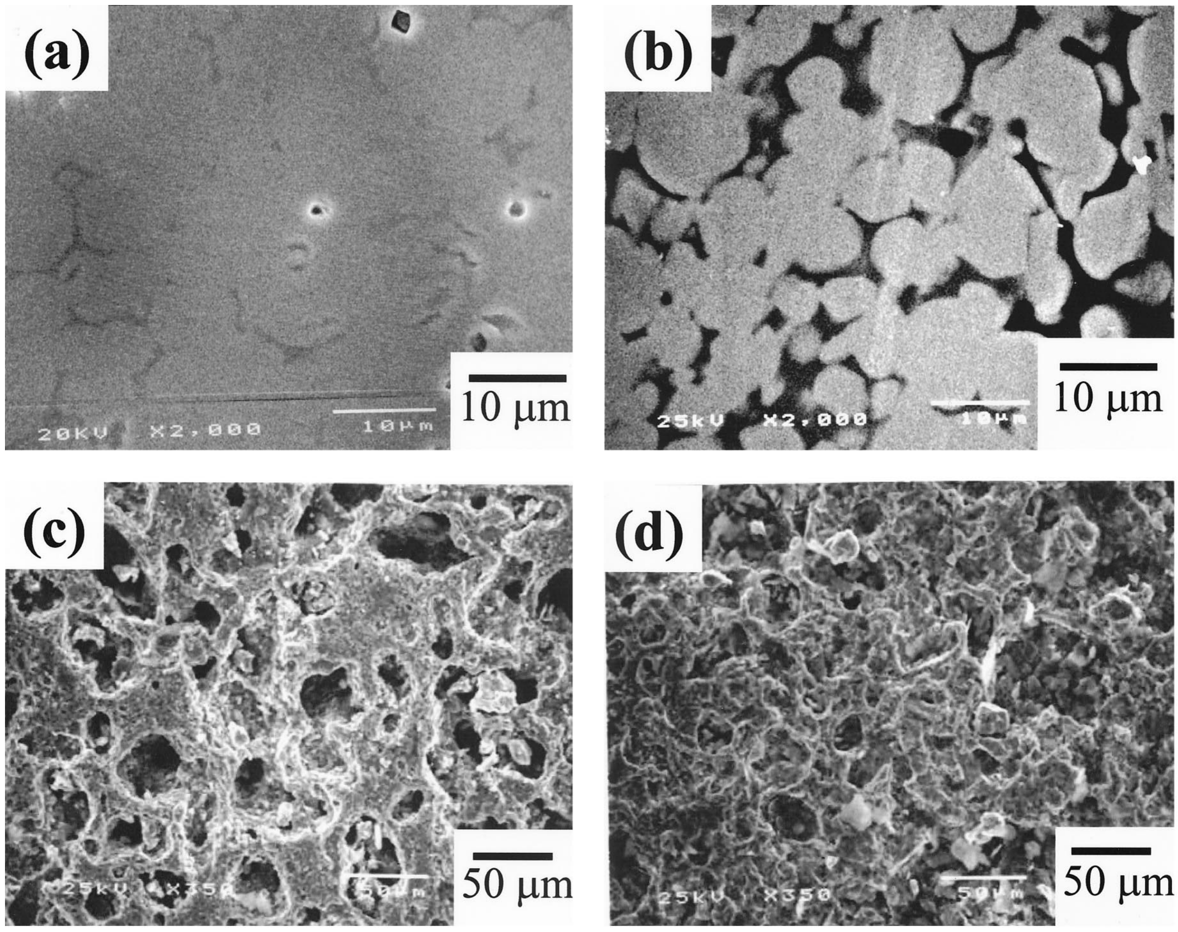

Fig. 5. SEM micrographs of polished product: (a) BN/Ti = 0.11, (b) BN/Ti = 0.25, (c) BN/Ti = 0.5, (d) BN/Ti = 1.0 (nitrogen pressure: 4.0 MPa).

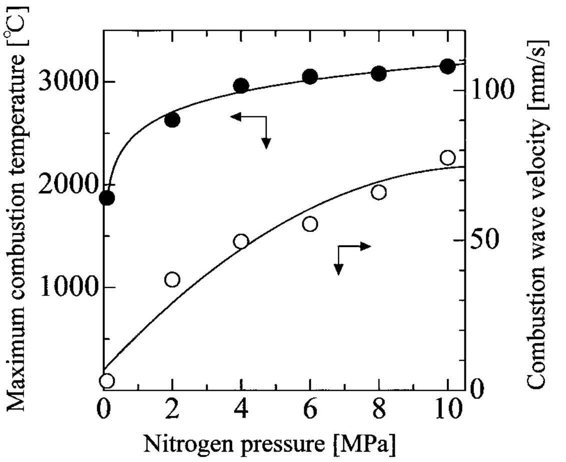

Fig. 7. Effect of nitrogen pressure on the maximum combustion temperature and combustion wave velocity (BN/Ti = 0.11).

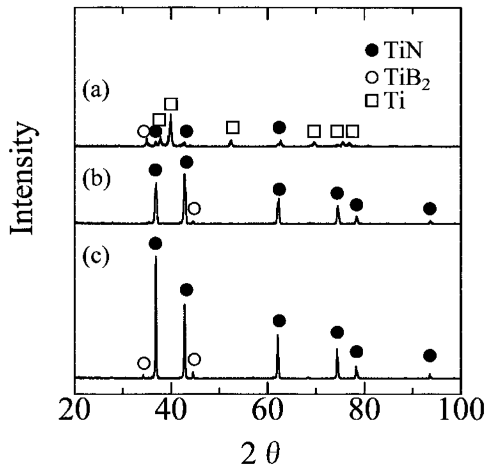

Fig. 9. XRD patterns of products synthesized at different nitrogen gas pressure: (a) 0.1, (b) 4.0, (c) 10 MPa (BN/Ti = 0.11).

relatively dense with no circumferential macrocracks. In the case of BN/Ti ratios of 0.33–1.0, the products were porous but had no cracks. The relative density of the product was calculated from a combination of the reported density for TiB_2, 4.50 $g\cdot cm^{-3}$, and the density calculated with the lattice parameter for TiN_x. The calculated density of TiN_x was 5.20 $g\cdot cm^{-3}$ at $x = 0.79$. The maximum bulk density of the product was 4.80 $g\cdot cm^{-3}$ for a BN/Ti ratio of 0.11. This value corresponds to a relative density of 92.6%. As indicated above, the products of samples with BN/Ti ratios higher than 0.33 were porous, with the degree of porosity increasing as this ratio was increased. The difference between the low and high BN content samples was related to the presence of a liquid phase. For samples with BN/Ti ratios in the range 0−0.25, the temperature was at or higher than the melting point of TiB_2. The presence of a liquid phase led to the formation of higher density product, as has been observed before in many investigations. In contrast, samples with BN/Ti ratios higher than about 0.3 had combustion temperatures lower than the melting point of TiB_2. Moreover, as indicated above, in samples with BN/Ti $\geq$ 0.67 nitrogen was produced rather than consumed during combustion. The generation of nitrogen led to further porosity generation, in a manner similar to the effect of impurity evolution.[20]

Evidence of melting can be seen from the SEM micrographs of the polished cross sections of products with BN/Ti ratios of 0.11 and 0.25 (Figs. 5(a) and (b)). The rounded particles of TiN (light gray) are surrounded by the TiB_2 phase (dark gray). The black regions are pores. These products were relatively dense, as indicated above. On the other hand, the products with BN/Ti ratios of 0.50 and 1.0 were porous, as shown in Figs. 5(c) and (d).

Figure 6 shows the effect of BN addition on the Vickers microhardness and on the fracture toughness, K_{IC}, of the relatively dense products ($0 \leq$ BN/Ti ≤ 0.3). The hardness showed a dependence on the BN/Ti ratio, exhibiting a maximum value of about 25 GPa at a ratio of 0.11. At this ratio the composite was dense and its TiB_2 content represented a value of 7.3 vol%. The fracture toughness of the products showed a weak dependence on BN addition, increasing from 3.1 to 5.9 $MPa\cdot m^{1/2}$ as the BN/Ti ratio increased from 0.10 to 0.20. The maximum microhardness value obtained for the dense products, 25 MPa (at a BN/Ti ratio of 0.11), was between the values reported for the pure phases: 33.0 and 20.1 GPa for TiB_2 and TiN, respectively.[21,22] Similarly, the maximum value for the fracture toughness obtained in this work, 5.9 $MPa\cdot m^{1/2}$ (at a BN/Ti ratio of 0.20) was in the range between the values of the pure phases. The fracture toughness for TiB_2 is reported as 6.4 $MPa\cdot m^{1/2}$ (Ref. 21) while that for TiN is reported to be in the range of 3.4−4.3 $MPa\cdot m^{1/2}$ (Refs. 22 and 23).

(2) Effect of Nitrogen Pressure at Constant BN Addition

Powder compacts with a BN/Ti ratio of 0.11 were reacted under nitrogen pressures ranging from 0.1 to 10 MPa. Figure 7 shows the effect of nitrogen pressure on the maximum combustion temperature and on the combustion wave velocity. Both parameters increased with increasing nitrogen pressure. It should be recalled that at this BN/Ti ratio, nitrogen is a reactant and the observed

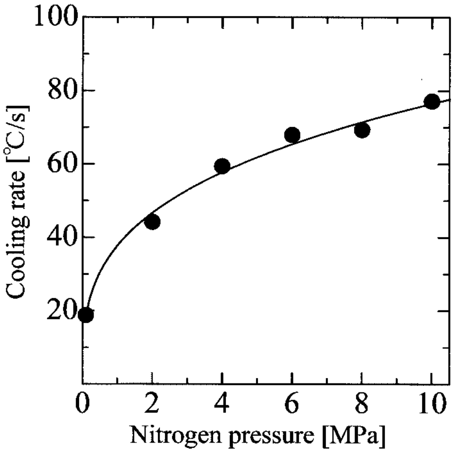

Fig. 8. Effect of nitrogen pressure on sample cooling rate (BN/Ti = 0.11).

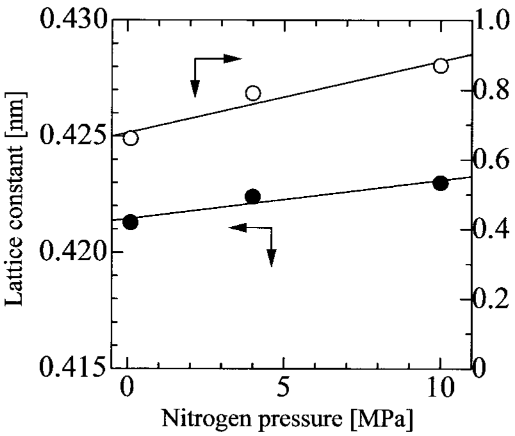

Fig. 10. Effect of nitrogen pressure on the lattice constant and x of TiN_x (BN/Ti = 0.11).

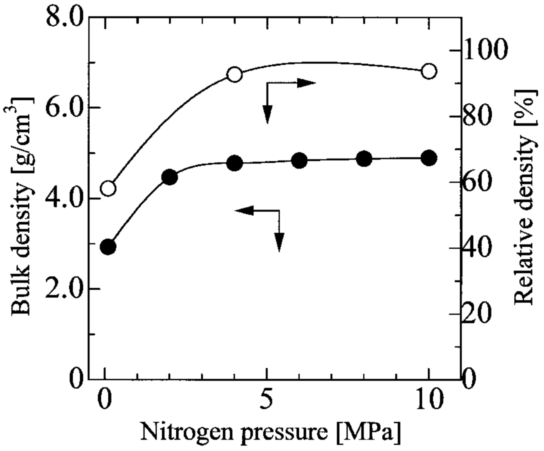

Fig. 11. Effect of nitrogen pressure on bulk relative densities of the products (BN/Ti = 0.11).

dependence on its pressure is consistent with general expectations. The maximum combustion temperature reached 3000°C under a nitrogen pressure of about 4.0 MPa and increased further as the pressure increased. The combustion wave velocity increased markedly from ~3.0 to 78 mm·s^{-1} as the nitrogen pressure increased from 0.1 to 10 MPa. The combustion wave velocity usually decreases with an increase in pressure due to convective heat loss, but in this case, the effect is dominated by the role of nitrogen as a reactant, as indicated above. A pressure increase signifies an increase in the local availability of nitrogen at the gas/solid interface. The increase in wave velocity is probably related to the enhancement of heat conduction by the presence of a molten phase. At pressures of 4.0 MPa or higher, the combustion temperature exceeds the melting point of TiB_2.

Circumferential macrocracks formed inside the fabricated products under a nitrogen pressure higher than 6.0 MPa. Figure 8 shows the effect of the nitrogen pressure on the cooling rate from the maximum temperature down to 1000°C. The cooling rate increased with an increase in nitrogen pressure, consistent with the role of a gas in convective heat loss, as stated above. For cases with pressures higher than 6.0 MPa, the cooling rate was higher than 60°C·s^{-1}. The presence of the cracks is thus likely to be the result of thermal shock for products synthesized under nitrogen pressures higher than 6.0 MPa.

Figure 9 shows X-ray diffraction patterns of the products under nitrogen pressure of (a) 0.1, (b) 4.0, and (c) 10 MPa. The products were identified as TiN_x and TiB_2. The peak intensity of TiN_x increased with increasing nitrogen pressure. Unreacted titanium was observed in the product under 1 atm (0.1 MPa) nitrogen pressure only, consistent with previous observations.[10] Figure 10 shows the effect of nitrogen pressure on the lattice constant and on x in TiN_x, as calculated from the XRD results. The x value of TiN_x increased with an increase in nitrogen pressure. For a pressure of 10 MPa, x was equal to 0.87. The effect of nitrogen pressure on the bulk and relative density of the products is shown in Fig. 11. In the pressure range between 0.1 and 4.0 MPa the density increased significantly, but with a further increase in the pressure, the density showed only a slight increase. At the highest pressure, 10 MPa, the density was 4.90 g·cm^{-3}, which correspond to a relative density of 94.0%, based on a nitride phase of $TiN_{0.87}$ as indicated by the XRD results. At a pressure of 4.0 MPa and higher, the temperature exceeds the melting point of TiB_2. Figure 12 shows SEM micrographs of cross-sectioned TiN/TiB_2 products obtained under nitrogen pressures of (a) 0.1, (b) 2.0, (c) 4.0, and (d) 10 MPa. The

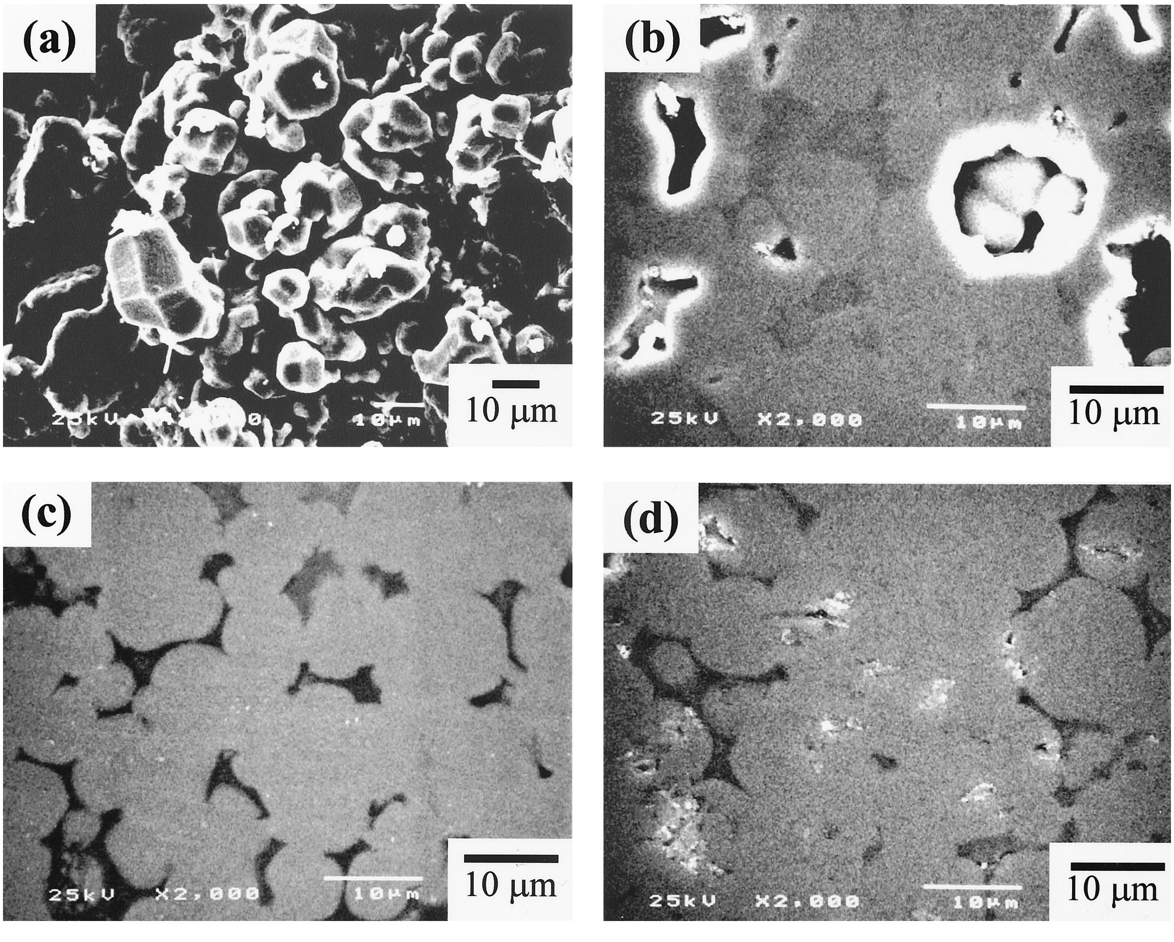

Fig. 12. SEM micrographs of products synthesized at different nitrogen gas pressure: (a) 0.1, (b) 2.0, (c) 4.0, (d) 10 MPa (BN/Ti = 0.11).

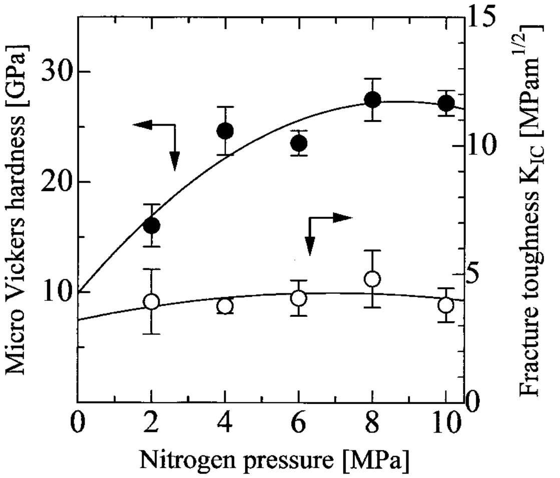

Fig. 13. Effect of nitrogen pressure on the Vickers microhardness and fracture toughness of the products (BN/Ti = 0.11).

products obtained under atmospheric nitrogen pressure were granular in appearance with morphologies indicative of the cubic structure of TiN and the hexagonal structure of TiB$_2$, as can be seen in Fig. 12(a). The combustion temperature is lower than the melting point of TiB$_2$ and the structure is distinctly different from that observed when TiB$_2$ is molten (see Fig. 5). In contrast, the microstructure of samples prepared under high nitrogen pressure (Figs. 12(c) and (d)) exhibits evidence of a molten phase. Here, the TiB$_2$ phase (dark gray) surrounds the TiN grains (light gray). The products synthesized under a nitrogen pressure of higher than 4.0 MPa were relatively dense. The particle size of TiN increased and the pore size decreased with an increase in nitrogen pressure. The former is a result of the effect of pressure on temperature.

The effect of nitrogen pressure on the Vickers microhardness and the fracture toughness of the products is shown in Fig. 13. The microhardness increased with nitrogen pressure in a manner consistent with the observed increase in density (Fig. 11). The microhardness of the product synthesized under a nitrogen pressure of 10 MPa was ~27 GPa. Fracture toughness measurements were also made on these samples. The results showed a slight increase of the toughness with nitrogen pressure. The fracture toughness K_{IC} values increased from 3.6 to 4.8 MPa·m$^{1/2}$ as the pressure increased from 2.0 to 10 MPa. The corresponding values of hardness and toughness for the component TiB$_2$ and TiN are, respectively, 33.0 and 20.1 GPa, and 6.4 and 3.4–4.3 MPa·m$^{1/2}$.[21–23]

IV. Conclusions

The present investigation demonstrates the feasibility of synthesizing (by combustion) composite materials with high hardness and toughness. Dense TiN/TiB$_2$ composites were fabricated by combustion synthesis with solid–solid and solid–gas reactions between elemental titanium, boron nitride, and gaseous nitrogen. Products free of macrocracks were obtained by controlling the BN addition and nitrogen pressure. The synthesized product from reactants with a BN/Ti mole ratio of 0.11 under a nitrogen pressure of 4.0 MPa had high hardness (25 GPa) and was free of macrocracks. However, samples synthesized under nitrogen pressures higher than 6.0 MPa contained macrocracks due to thermal shock.

Acknowledgments

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